Journal of Petroleum Science and Engineering 156 (2017) 12–18

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Qualitative and quantitative analysis of oil samples extracted from some Bashkortostan and Tatarstan oilfields based on NMR spectroscopy data

I.Z. Rakhmatullin, S.V. Efimov, B.Ya. Margulis, V.V. Klochkov *

Kazan Federal University, 18 Kremlevskaya St., 420008 Kazan, Russian Federation

ARTICLE INFO

Keywords:
^{1}H NMR spectroscopy
^{13}C NMR spectroscopy
Crude oil
Functional group
Qualitative analysis
Quantitative composition

ABSTRACT

Measurements of crude oil samples by nuclear magnetic resonance spectroscopy were carried out. The quantitative fractions of aromatic molecules and functional groups constituting oil hydrocarbons in several samples were determined and their slight variation from sample to sample was shown. Information on content of general functional groups (tertiary and primary carbon atoms, aromatic cores) and possible presence of olefins or water impurity can be obtained. Basic ^{1}H measurements are rather fast and require several minutes. Experiments on modern high-field spectrometers provide better resolution of overlapping regions in ^{13}C NMR spectra and thus would be more convenient to get detailed information on the amount of different alkyl substituents. Slight but obvious differences were observed between the spectra of the samples taken from different levels of the same oil well.

1. Introduction

Knowledge of the chemical composition and physicochemical properties of crude oils, along with features of the geological and geochemical conditions, is of primary importance for solving problems of the origin of crude oils and for petroleum refining, since it enables variations in the commercial and technical characteristics of crude oils to be predicted and the expediency of combining crude oils from different fields during refining to be assessed (Kvalheim et al., 1985).

Petroleum as a natural object contains hundreds of substances mainly belonging to the three homologous series of hydrocarbons (alkanes, cycloalkanes, and aromatic hydrocarbons), as well as heteroatomic compounds (particularly, asphaltene-resinous substances) containing non-metals (sulfur, oxygen, nitrogen) and trace elements (V, Ni, Fe, Zn, etc.) (Speight, 2014; Pokonova et al., 1984; Van Ness and Van Westen, 1951). Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties and ultimately its behavior during refining. Structural recognition of the oil constituents is the prerequisite of different techniques used for heavy oil upgrading. In contrast to other physical-chemical methods (De Peinder et al., 2008; Satya et al., 2007; Jehlička et al., 2003; Sjoblom et al., 1998), nuclear magnetic resonance (NMR) spectroscopy allows obtaining both qualitative (type of molecules) and quantitative (content of compounds) information on a mixture of organic compounds. The history of ^{1}H and ^{13}C NMR spectroscopy shows that application of these techniques for compositional characterization of petroleum fractions was a breakthrough and was considered a novel development in this area (McLean and Kilpatrick, 1997; Trejo et al., 2004).

There are many methods for investigation of oil composition including gas chromatography and quantitative fluorescence techniques (Xixian et al., 2000; Fuhua et al., 2001a, 2001b; Xiexian et al., 2003; Xingli et al., 2007). Although these methods can resolve some problems, they can only qualitatively describe the fluorescence characteristics based on the variable chromatography curves (Zhizhan et al., 2015).

NMR has the advantage to provide directly molecular details determining physical-chemical properties of a sample at a macroscopic level (Lintelmann, 1995). In fact, an NMR spectrum contains information in terms of the molecular functional groups and, if recorded with the proper resolution, may allow characterizing a sample at the molecular level (Allen et al., 1985; Behera et al., 2008). Modern NMR spectroscopy technique is based not only on increased sensitivity and resolution, but also applies two-dimensional methods, which provide additional information on the composition of oil samples from NMR spectra. Taking into account the importance of oil to the economy, there is a very important and urgent task for adaptation of modern 1D NMR (^{1}H, ^{13}C) and 2D NMR (COSY, HSQC experiments) spectroscopy to determination of oil composition.

^{1}H NMR spectroscopy is a relatively fast method, which does not

* Corresponding author.
E-mail address: vladimir.klochkov@kpfu.ru (V.V. Klochkov).

http://dx.doi.org/10.1016/j.petrol.2017.04.041
Received 15 July 2016; Received in revised form 10 April 2017; Accepted 27 April 2017
Available online 28 April 2017